

Redox state of the Archean atmosphere: Evidence from detrital heavy minerals in ca. 3250–2750 Ma sandstones from the Pilbara Craton, Australia

Birger Rasmussen

Centre for Strategic Mineral Deposits, Department of Geology and Geophysics,
University of Western Australia, Nedlands, WA 6907, Australia

Roger Buick

School of Geosciences, Edgeworth David Building F05,
University of Sydney, Sydney, NSW 2006, Australia

ABSTRACT

The presence of detrital uraninite and pyrite in fluvial placers of the Witwatersrand basin, South Africa, has been used to infer low levels of atmospheric oxygen during the Archean (>2500 Ma). However, recent studies advocate a hydrothermal origin for these minerals, thereby limiting their value as constraints on the composition of the early atmosphere. In contrast, ca. 3250–2750 Ma fluvial siliciclastic sediments from the Pilbara Craton in Australia have never undergone significant hydrothermal alteration, and their heavy minerals are of unequivocal detrital origin. These heavy minerals include the redox-sensitive phases pyrite, uraninite, and gersdorffite, along with more inert zircon, rutile, chromite, and monazite. Locally, siderite is a major constituent (to 90%) of the heavy mineral population, with grains displaying evidence for several episodes of erosion, rounding, and subsequent authigenic overgrowth. Detrital siderite is very rare in post-Archean sandstones, largely due to its instability in oxidizing environments. However, its frequent survival of prolonged transport in well-mixed and therefore well-aerated Archean river waters that contained little organic matter strongly implies that the contemporary atmosphere was indeed much less oxidizing than at present. Moreover, concentrations of reduced sulfur species must have been very low in surface fluids for siderite to survive repeated transportation events without pyritization.

INTRODUCTION

It is widely accepted that the surface environment of the Archean Earth was less oxidizing than now (e.g., Des Marais, 1994). However, this has been difficult to prove, let alone quantify, so much so that a small but significant group of scientists maintains that redox conditions in the Archean hydrosphere and atmosphere did not differ greatly from those prevailing today (Clemmey and Badham, 1982; Towe, 1991; Ohmoto, 1996). It is not a trivial dispute, as the issue bears upon the temporal distribution of economic minerals and the evolutionary history of microbial organisms.

Geological indicators of less-oxidizing Archean environments include the absence of red-beds, the existence of banded iron-formations, the prevalence of iron-depleted paleosols, and the occurrence of unusual detrital minerals. Particularly important is the purported presence of detrital uraninite and pyrite in the Witwatersrand basin of South Africa (Ramdohr, 1958; Schidlowski, 1981) as this has provided some of the best quantitative estimates ($<10^{-2}$ present atmospheric level [PAL]) of atmospheric O_2 during the Archean (Grandstaff, 1980; Holland, 1984). However, many workers (e.g., Phillips et al., 1987; Barnicoat et al., 1997) advocate a hydrothermal mode of formation for these minerals, in which case the

minerals would indicate little or nothing about surficial environments.

With that debate in mind, this paper attempts to constrain the composition of the atmosphere during part of the Archean (ca. 3250–2750 Ma) using heavy mineral suites in terrestrial sandstones from the Pilbara Craton of Australia. There, metamorphism has been less severe and hydrothermal alteration less intense than in similarly ancient rocks elsewhere, so a detrital origin for the heavy minerals is less equivocal. The most significant of these minerals is siderite, a highly redox-sensitive phase that has not previously been described as a detrital component of Archean sedimentary rocks. From its petrologic relationships and sedimentary setting, it evidently survived prolonged transport in well-aerated water and can therefore be used as an indicator of the composition of the ambient atmosphere.

Methods

Four sandstone-conglomerate successions in the Pilbara Craton (Table 1) spanning ca. 3250–2750 Ma were sampled from diamond-drill core and outcrop. Polished thin sections (~100) were examined with a polarizing microscope, and a JEOL JSM-6400 scanning microscope equipped with a Link Systems energy-dispersive X-ray microanalyzer.

Geologic Setting

Fortescue Group sandstones were deposited between 2770 and 2715 Ma in a series of north-northeast-trending half-grabens created during the early stages of a continental breakup event (Blake, 1993). The sandstones were deposited by braided rivers that flowed for many tens of kilometers parallel to the structural trend (Blake, 1993). The trough-cross-bedded sandstones are mature, moderately to well sorted, and consist of rounded quartz with minor feldspar, lithic fragments, and heavy minerals. Framework grains are surrounded by quartz cement and sericite matrix, the latter significantly devoid of organic matter. Heavy minerals (Table 1) are concentrated in seams along foreset planes and scour surfaces. Uraninite and thorite occur as inclusions within bitumen nodules. The rocks are only slightly deformed, and metamorphism never exceeded prehnite-pumpellyite facies (Smith et al., 1982). Other postdepositional alteration has been negligible.

The Lalla Rookh Formation was deposited in a strike-slip basin ca. 3000–2950 Ma (Krapez, 1996). The axial region of the basin contained a braided-river system many tens of kilometers long that flowed into a terminal lake and was fed by marginal alluvial fans (Krapez, 1996). The fluvial sandstones are trough-cross-bedded, mod-

TABLE 1. HEAVY MINERAL ASSEMBLAGES IN ARCHEAN CONGLOMERATE-SANDSTONE SUCCESSIONS FROM THE PILBARA CRATON

Sedimentary formation	Average concentration of heavy mineral species (%)								
	Pyrite	Fe-oxides*	Fe-Co-Ni:As-S	Siderite	Uraninite	Zircon	Ti-oxides†	Chromite	Miscellaneous‡
Fortescue Group									
Nullagine	30	0	<1	55	1	3	10	<1	<1
West Pilbara	80	10	0	0	0	<1	5	<1	4
Lalla Rookh Formation	55	0	<1	<1	0	10	5	25	4
Dromedary Hills sequence	65	0	<1	0	<1	10	2	15	7

* Iron oxide rims after pyrite grains weathered in the modern atmosphere.

† Skeletal titanium oxides after altered ilmenite and titanomagnetite grains.

‡ Miscellaneous heavy minerals include rutile, monazite, apatite, xenotime, garnet, thorite, and allanite.

erately to well sorted, mature quartz arenites, with minor feldspar, lithic fragments, and heavy minerals. Framework grains are subrounded to rounded, and are set in quartz cement and kero-gen-free sericite matrix. Heavy minerals (Table 1) are concentrated on foresets and horizontal laminae in bar and channel facies. Their host rocks are metamorphosed to prehnite-pumpel-lyte facies and lack evidence of hydrothermal al-teration. Some postdepositional silicification has occurred near faults and in condensed sections.

The Dromedary Hills sequence of the Mos-quito Creek Formation is a structurally bounded succession deposited in a forearc basin about 3250 Ma (Eriksson et al., 1994). The rocks, now schists and quartzites, have been silicified, meta-morphosed to greenschist grade, and isoclinally folded. Originally, however, they were coarsen-ing-upward beds of sandstone and conglomerate apparently forming bar-channel associations in a fluviodeltaic environment (Eriksson et al., 1994). The dimensions of the sediment transport system are unknown due to structural disruption. The sandstones are relatively mature, moderately sorted, and contain subangular to rounded quartz with minor feldspar, lithic fragments, and heavy minerals in a quartz cement and a sericite-chlo-rite matrix. Heavy minerals (Table 1) are concen-trated in bar facies.

REDOX-SENSITIVE HEAVY MINERALS

Pyrite and Other Sulfides

Pyrite is typically the most abundant heavy mineral (Table 1). The grains (average 0.3 mm in size) are mostly subrounded to rounded and com-monly display complex compositional banding which is truncated at grain boundaries (Fig. 1A). Subangular to rounded Fe-Ni-Co sulfide and sul-farsenide grains, most notably gersdorffite, are also present in low abundance (Table 1) and are similar in size to adjacent pyrite grains. In out-crop samples, rounded sulfide and sulfarsenide grains are partly to entirely replaced by Fe-ox-ides, a modern weathering phenomenon.

Uraninite

Uraninite occurs in the Dromedary Hills se-quence and the Fortescue Group. In the former,

subangular to subrounded grains are rare con-stituents of heavy mineral seams. Minute blocky inclusions (<10 μ m) are also scattered through the bitumen nodules prevalent in such laminae. These inclusions are apparently relics of detrital uraninite grains that were fragmented during dia-genesis by bitumen growth along intragranular fractures as a result of radiation-induced poly-merization of fluid hydrocarbons (Buick et al., 1998). In the Fortescue Group, uraninite is solely present as inclusions in bitumen nodules.

Siderite

Siderite grains are present in the Fortescue Group and Lalla Rookh Formation (Table 1), where they form the main component of some heavy mineral seams (Fig. 1B). Most grains range in size from 0.1 to 1.0 mm (average ~0.4 mm) and are now angular, although their current size and shape result from syntaxial overgrowth by diagenetic siderite (Fig. 1C). Backscattered electron (BSE) images show that most siderite grains contain a spherical to oval, subrounded to well-rounded core which displays complex com-positional banding (Fig. 1D and E). These inter-nal bands are truncated at the rounded core boundary by an outer rim that has itself been partly rounded. In places, the rim contains concn-tric bands of fluid inclusions (Fig. 1F). Evi-dently, the rounded cores were primary detrital grains around which siderite precipitated during early diagenesis, only to be exhumed, trans-ported, rounded, deposited, and overgrown again.

DISCUSSION

Detrital Origin

Although authigenic pyrite and siderite crys-tals are present in samples from the Pilbara Craton, a detrital origin can be readily demon-strated for most of these redox-sensitive con-stituents. Important criteria for recognizing detri-tal minerals include appropriate relative size of grains of differing density (indicating attainment of hydraulic equivalence), appropriate relative rounding of grains of differing hardness (indicat-ing equivalent degrees of abrasion), truncation of internal compositional zoning by rounded sur-faces (indicating abrasive rather than accretional

or dissolutional rounding), strong sedimentolog-ical control of grain distribution (concentrated on bedding planes or erosional surfaces), and inti-mate association with rounded grains of inert heavy minerals (zircon or chromite). All rounded siderite, pyrite, and other sulfide grains in the Pil-bara samples satisfy most, if not all, of these cri-teria, so their detrital origin is unequivocal. The only phase of doubtful origin is the uraninite in the Fortescue samples, consisting solely of inclu-sions in bitumen nodules. However, by analogy to similar material in the Dromedary Hills se-quence that clearly represents fragmented detrital grains, a detrital precursor can also be inferred for these. The alternative possibility, precipitation from an oxidized hydrothermal fluid that was re-duced by a hydrocarbon phase (cf. Gray et al., 1998), is unlikely, because there is no other evi-dence of uranium mobility and similar fragmen-tation textures occur in nodules containing the re-fractory radioactive mineral thorite.

Provenance and Preservation

Many factors other than water chemistry affect the composition of redox-sensitive detrital min-eral assemblages preserved in sedimentary rocks (Morton, 1985), particularly the topography and climate of the provenance area. For example, in arid, glacial, or montane environments, rates of chemical weathering may be substantially re-duced, allowing minerals normally unstable under ambient conditions to survive in clastic sediments close to their source. In the Pilbara Craton, the proximity of the source region is unknown only for the Dromedary Hills sequence. For the Fortes-cue and Lalla Rookh samples, there is no strong evidence of highly arid or glacial conditions, but a rugged source terrain is indicated by steep slopes on erosion surfaces, talus breccias, and debris-flow deposits (Blake, 1993; Krapez, 1996). How-ever, none of the samples came from such prox-i-mal deposits, so some transportation away from the source region has occurred.

Transport History

Different mineral phases in the Pilbara sam-ples have probably undergone varying amounts of transportation. Uraninite, pyrite, and gersdorff-

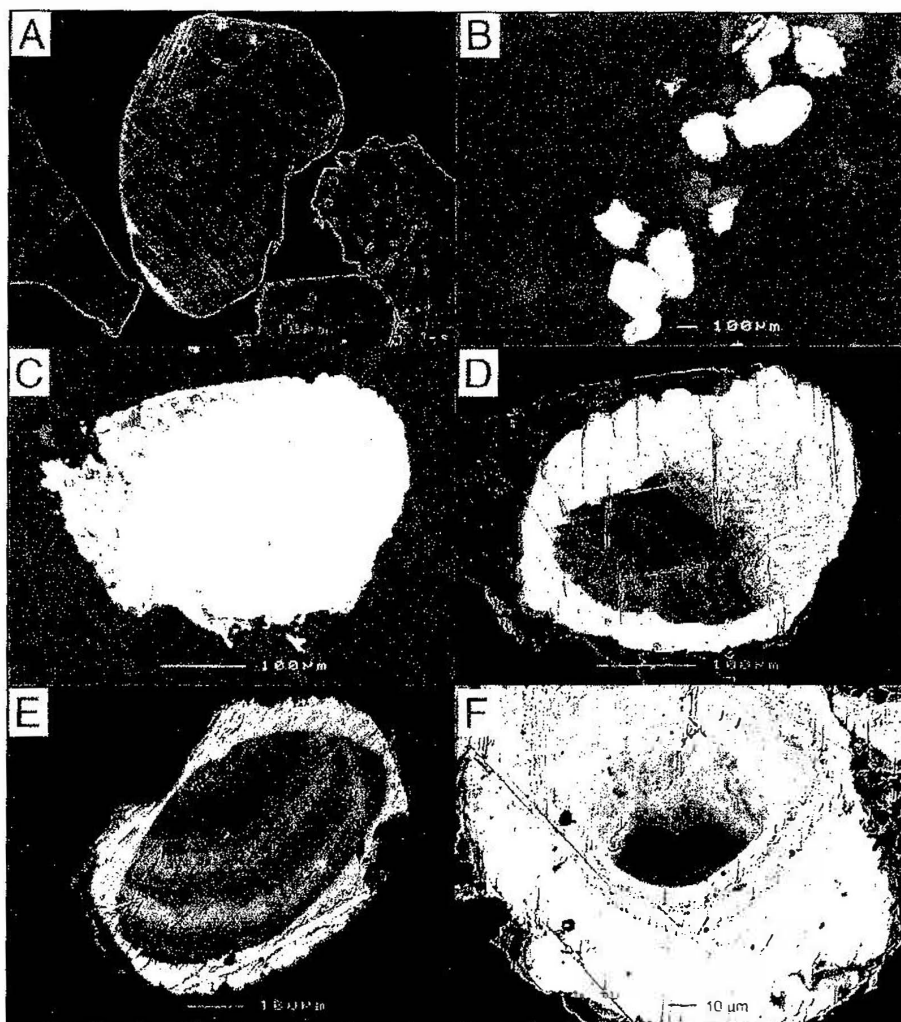


Figure 1. A: Rounded pyrite grain with compositional banding truncated at grain surfaces. Backscattered electron (BSE) image, Dromedary Hills sequence. B: Heavy mineral band of siderite (light gray) with syntaxial overgrowths (medium gray), zircon (white), and pyrite (white). BSE image, Fortescue Group, Nullagine sub-basin. C: Closeup of rounded siderite grain with syntaxial overgrowths (gray to black). BSE image, Fortescue Group, Nullagine sub-basin. D: Same as C, using high-contrast BSE imaging that reveals a rounded core of compositionally banded siderite. Note truncation of banded core. BSE image, Fortescue Group, Nullagine sub-basin. E: Rounded siderite grain, with core of compositionally banded siderite and syntaxial overgrowths (gray to black). BSE image, Fortescue Group, Nullagine sub-basin. F: Closeup of siderite grain with banded core truncated by outer rim of concentric bands (~25 μm thick). BSE image, Fortescue Group, Nullagine sub-basin.

fit are all relatively resistant to abrasion, having hardnesses of 5 or more on the Mohs scale. Because they are generally well rounded, at least as much as accompanying quartz, they were probably in transport for a considerable time. Siderite, which is quite soft (3.75–4.25 hardness), might not be expected to survive prolonged transport in quartz-dominated fluvial bedload. However, similarly soft and brittle minerals such as wolframite and xenotime are reasonably abundant detrital phases in modern mature quartzose sands. Moreover, the Pilbara siderite shows evidence of two episodes of erosion, transportation and deposition in the form of rounded overgrowths over the original rounded grain cores, indicating transportation over substantial distances. So, because

the Pilbara sedimentary basins contained lengthy river systems and the heavy mineral samples are not notably proximal to source, all redox-sensitive heavy minerals probably traveled many kilometers before ultimate deposition.

Atmospheric Equilibration

The braided rivers that transported the Pilbara sandstones were turbulent, shown by the abundance of trough-cross-bedding, and hence, would have been well aerated. They evidently carried a negligible load of organic particulates, as sandstone matrices are kerogen-free. If dissolved organic compounds were similarly scarce, as they probably were, the redox state of the river water should reflect that of the atmosphere. So,

detrital minerals would have had ample opportunity for reaction with dissolved atmospheric gases while being transported as fluvial bedload, especially the siderite grains that underwent several episodes of transport. Evidently then, redox reaction kinetics were quite slow due to low atmospheric partial pressures of oxidizing gases, thus reducing rates of reactive mineral destruction in the detrital assemblage.

Pyrite and Uraninite

Detrital pyrite and uraninite are very rare in sedimentary rocks younger than ca. 2000 Ma, being mostly restricted to cold climates where chemical weathering is retarded or to mountainous terrains where immature sediments are rapidly deposited (e.g., upper reaches of the Indus River; Maynard et al., 1991). Their scarcity may be explained by the physical and chemical instability of both minerals in oxidizing conditions (Holland, 1984). Due to this redox sensitivity, the apparent detrital origin of uraninite and pyrite grains in Archean sandstones, particularly those of the auriferous Witwatersrand Supergroup of South Africa (e.g., Ramdohr, 1958; Smith and Minter, 1980; Reimer and Mossman, 1990), has been used to constrain atmospheric oxygen levels at the time of sediment deposition. Most notably, Grandstaff (1980) estimated that atmospheric P_{O_2} (P = partial pressure) must have been below 10^{-2} to 10^{-6} PAL for detrital uraninite to survive.

Recently, however, the detrital origin of Witwatersrand uraninite and pyrite has been seriously questioned (e.g., Phillips et al., 1987; Bamicoat et al., 1997), thereby casting doubt on the validity of these estimates. The revisionists argue that the rounded pyrite grains represent detrital Fe-oxide and Fe-silicate grains that were pyritized in situ by sulfur-bearing hydrothermal fluids. They consider that all uraninite formed after sediment deposition when uranium-rich hydrothermal fluids reacted with hydrocarbons or preexisting minerals, causing precipitation. As there is strong evidence for at least some secondary pyrite and uraninite formation in these rocks, such arguments cannot be lightly dismissed.

Given the problems with the Witwatersrand evidence, heavy mineral suites in unmineralized rocks may add significantly to the debate. Archean siliciclastic successions of the Pilbara Craton are generally poor in U and Au, with no evidence for hydrothermal mineralizing events. Because the major redox-sensitive minerals in these successions, pyrite with locally significant uraninite, are evidently detrital, they were capable of lengthy survival in the contemporary surficial environment. Thus, the Grandstaff estimates still stand, even if on different foundations.

Siderite

Siderite is extremely rare as a detrital component of sedimentary rocks, particularly sandstone (Milner, 1962). Its modern detrital occur-

rences are generally limited to angular grains in highly immature sediments derived from largely unweathered terrains and deposited very close to their source (Davidson and Cosgrove, 1955; Mange and Maurer, 1992). Its general absence is due to its instability in oxic conditions, where it rapidly reacts with free O_2 to form ferric oxides (Bernier, 1981). Hence, siderite is highly unlikely to survive prolonged weathering and transport under contemporary atmospheric conditions.

The absence of detrital siderite grains in siliciclastic sediments of the Witwatersrand and Huronian Supergroups has been used to infer the chemical instability of siderite in Archean fluvial environments, and thereby to constrain the chemistry of the atmosphere (Krupp et al., 1994). However, as noted here, detrital siderite grains are locally abundant in several Pilbara siliciclastic successions. Moreover, they occur in cross-bedded braided-stream deposits, which indicates transportation in fast-flowing, turbulent water that was well mixed with the atmosphere. They were carried a considerable distance in this well-aerated medium and some persisted through two cycles of weathering, transportation, and diagenesis. This strongly suggests that siderite was only slowly chemically degraded in Archean river water and thus that the atmosphere was less oxidizing.

CONCLUSIONS

Under modern conditions, uraninite, pyrite, and siderite are rapidly oxidized upon exposure to the atmosphere, and rarely survive as detrital components in sediments or sedimentary rocks. In the Pilbara sandstones, the absence of any signs of chemical reaction between these redox-sensitive heavy minerals and the ambient fluids suggests a markedly different scenario. The persistence of these minerals as detrital grains during prolonged transportation in organic-poor fluvial environments indicates that Archean river water, and hence the early atmosphere, was significantly less oxidizing than now (possibly $<10^{-6}$ moles per liter; Bernier, 1981). As the rivers were evidently turbulent and thus well-aerated, the Archean atmosphere was almost certainly less oxygenated too. Siderite is also unstable in the presence of reduced sulfur, readily forming pyrite, so H_2S concentrations in weathering profiles and surface waters must also have been very low. This implies atmospheric H_2S levels $<10^{-5}$ atm for all likely values of P_{CO_2} and P_{H_2} in the Archean atmosphere (Holland, 1984, p. 107).

These conclusions bear out the mounting geologic evidence from palcosols and sedimentary precipitates for a less-oxidizing Archean atmosphere (Rye and Holland, 1998). This is supported further by isotopic data from biogeochemical elements that indicate major changes in their cycling since ca. 2700 Ma (Hayes, 1994). It is difficult to determine how much less oxidizing

the Archean atmosphere was, because most indicators are at best semiquantitative (Holland, 1994). However, detailed thermodynamic and kinetic studies of siderite stability with respect to Eh, pH, P_{CO_2} and P_{H_2} should yield more precise estimates of Archean P_{O_2} because this mineral is particularly sensitive to the redox state of the environment.

ACKNOWLEDGMENTS

We thank G. Ellis, T. S. Blake, and B. Krapez for samples; T. S. Blake, B. Krapez, E. Mikucki, and M. Hughes for advice; B. Krapez, H. D. Holland, and N. J. Beukes for reviews; and B. J. Griffin, G. Pooley, and J. Hilyer for analytical help. This study was supported by the Australian Research Council by way of a Postdoctoral Research Fellowship to Rasmussen and Large Grant A39600061 to Buick.

REFERENCES CITED

- Barnicoat, A. C., Henderson, I. H. C., Knipe, R. J., Yareley, B. W. D., Napier, R. W., Fox, N. P. C., Kenyon, A. K., Munthigh, D. J., Strydom, D., Winkler, K. S., Lawrence, S. R., and Cornford, C., 1997, Hydrothermal gold mineralization in the Witwatersrand basin: *Nature*, v. 386, p. 820–824.
- Bernier, R. A., 1981, A new geochemical classification of sedimentary environments: *Journal of Sedimentary Petrology*, v. 51, p. 359–365.
- Blake, T. S., 1993, Late Archean crustal extension, sedimentary basin formation, flood basalt volcanism and continental rifting: The Nullagine and Mount Ipe Supersequences, Western Australia: *Precambrian Research*, v. 60, p. 185–241.
- Buick, R., Rasmussen, B., and Krapez, B., 1998, Archean oil: Evidence for extensive hydrocarbon generation and migration 2.5–3.5 Ga: *American Association of Petroleum Geologists Bulletin*, v. 82, p. 50–69.
- Clemmey, H., and Badham, N., 1982, Oxygen in the Precambrian atmosphere: An evaluation of the geological evidence: *Geology*, v. 10, p. 141–146.
- Davidson, C. F., and Cosgrove, M. E., 1955, On the impersistence of uraninite as a detrital mineral: *Great Britain Geological Survey Bulletin*, v. 10, p. 74–80.
- Des Marais, D. J., 1994, The Archean atmosphere: Its composition and fate, in: *Condie, K. C., ed., Archean crustal evolution: Developments in Precambrian Geology 11: Amsterdam, Elsevier*, p. 505–523.
- Eriksson, K. A., Krapez, B., and Fralick, P. W., 1994, Sedimentology of Archean greenstone belts: Signatures of tectonic evolution: *Earth-Science Reviews*, v. 37, p. 1–88.
- Grandstaff, D. E., 1980, Origin of uraniferous conglomerates at Elliot Lake, Canada, and Witwatersrand, South Africa: Implications for oxygen in the Precambrian atmosphere: *Precambrian Research*, v. 13, p. 1–26.
- Gray, G. J., Lawrence, S. R., Kenyon, K., and Cornford, C., 1998, Nature and origin of "carbon" in the Archean Witwatersrand Basin, South Africa: *Geological Society of London Journal*, v. 155, p. 39–59.
- Hayes, J. M., 1994, Global methanotrophy at the Archean-Proterozoic transition, in: *Bengtson, S., ed., Early life on Earth: Nobel Symposium 84: New York, Columbia University Press*, p. 220–236.

- Holland, H. D., 1984, *The chemical evolution of the atmosphere and oceans*: Princeton, New Jersey, University Press, Princeton, 582 p.
- Holland, H. D., 1994, Early Proterozoic atmospheric change, in: *Bengtson, S., ed., Early life on Earth: Nobel Symposium 84: New York, Columbia University Press*, p. 237–244.
- Krapez, B., 1996, Sequence stratigraphic concepts applied to the identification of basin-filling rhythms in Precambrian successions: *Australian Journal of Earth Sciences*, v. 43, p. 355–380.
- Krupp, R., Oberthür, T., and Hirdes, W., 1994, The early Precambrian atmosphere and hydrosphere: Thermodynamic constraints from mineral deposits: *Economic Geology*, v. 89, p. 1581–1598.
- Mange, M. A., and Maurer, H. F. W., 1992, *Heavy minerals in colour*: London, Chapman and Hall, 147 p.
- Maynard, J. B., Ritzer, S. D., and Sutton, S. J., 1991, Chemistry of sands from the modern Indus River and the Archean Witwatersrand basin: Implications for the composition of the Archean atmosphere: *Geology*, v. 19, p. 265–268.
- Milner, H. B., 1962, *Sedimentary petrography, Volume 2, Principles and Applications*: New York, Macmillan Inc., 715 p.
- Morton, A. C., 1985, Heavy minerals in provenance studies, in: *Zuffa, G. G., ed., Provenance of arenites*: Dordrecht, D. Reidel, p. 249–278.
- Ohmoto, H., 1996, Evidence in pre-2.2 Ga palcosols for the early evolution of atmospheric oxygen and terrestrial biota: *Geology*, v. 24, p. 1135–1138.
- Phillips, G. N., Myers, R. E., and Palmer, J. A., 1987, Problems with the placer model for Witwatersrand gold: *Geology*, v. 15, p. 1027–1030.
- Ramdohr, P., 1958, New observations on the ores of the Witwatersrand in South Africa and their genetic significance: *Geological Society of South Africa Transactions*, v. 61, p. 1–50.
- Reimer, T. O., and Mossman, D. J., 1990, The Witwatersrand controversy revisited: *Economic Geology*, v. 85, p. 337–343.
- Rye, R., and Holland, H. D., 1998, Palcosols and the evolution of atmospheric oxygen: A critical review: *American Journal of Science* (in press).
- Schidlowski, M., 1981, Uraniferous constituents of the Witwatersrand conglomerates: Ore-microscopic observations and implications for Witwatersrand metallogeny: *U.S. Geological Survey Professional Paper 1161*, p. N1–N29.
- Smith, N. D., and Minter, W. E. L., 1980, Sedimentological controls of gold and uranium in two Witwatersrand paleoplacers: *Economic Geology*, v. 75, p. 1–14.
- Smith, R. E., Perdrix, J. L., and Parks, T. C., 1982, Burial metamorphism in the Hamersley Basin, Western Australia: *Journal of Petrology*, v. 23, p. 75–102.
- Towe, K. M., 1991, Aerobic carbon cycling and cerium oxidation: Significance for Archean oxygen levels and banded iron-formation deposition: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 97, p. 113–123.

Manuscript received June 25, 1998

Revised manuscript received September 28, 1998

Manuscript accepted October 14, 1998